Biogeochemistry of Seasonally Snow-Covered Catchments (Proceedings of a Boulder Symposium, July 1995). IAHS Publ. no. 228, 1995.

Hydrochemical processes during snowmelt in a subalpine watershed, Colorado, USA

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Abstract Snowmelt is the primary hydrologic event in the studied subalpine watershed, generating streamflow for 3 months from a 1-month snowmelt period which commenced in mid-April 1992 and mid-May 1993. The melting rate of the snowpack varied diurnally and was asymmetrical, increasing rapidly to a maximum at the onset of daily melt followed by an attenuated decrease. Streamflow varied diurnally, displaying a similar pattern to that of snowmelt, but variations were much less marked. Groundwater levels also varied diurnally, but were more attenuated than that of streamflow, and the time of daily maximum coincided with the streamflow maximum, whereas the snowmelt maximum preceded them. The major ions in meltwater were preferentially eluted from the snowpack, and meltwater was dominated by calcium, sulfate, and nitrate. The concentration decreases observed in snowmelt are partially reflected in stream water. Groundwater was dominated by calcium and generally bicarbonate. Concentrations of weathering products (silica, alkalinity, and base cations) increased down gradient, consistent with an increase in water residence time. A watershed mass balance for 1992 and 1993 indicates that (1) a major percentage of the primarily atmospherically derived N-species are retained by the watershed, (2) the watershed is the major source of base cations and silica, and (3) for the 2 year combined, atmospheric deposition balances stream water transport of sulfate and chloride.

INTRODUCTION

Snow accumulation and melt are the dominant hydrologic processes that provide most of the water to ecosystems in the western mountain ranges of the United States. Hydrologic and hydrochemical processes occurring in the snowpack and to meltwater as it travels through a watershed are not well understood. Flow routing and biotic and abiotic processes occurring along hydrologic pathways can have a major effect on the chemical composition and transport of solutes during snowmelt.

Surface water in the mountains of Colorado and other areas of the western United States is relatively dilute, particularly when compared to surface water in mountainous areas draining similar bedrock lithologies in the eastern United States. Increasing industrial and urban development of the western United States could affect hydrochemistry of these waters through changes in the chemistry of atmospheric deposition.

The objective of this paper is to evaluate major solute concentrations and fluxes in water as it travels through a subalpine watershed in the Rocky Mountains during snowmelt 1992 and 1993; selected results of the data analysis are also presented. The watershed is at Rabbit Ears Pass in the North Fork Walton Creek basin at 40°39′13″N and 107°4′35″W (Fig. 1). Basin characteristics are listed in Table 1 and methods are described by Peters & Leavesley (1994).

HYDROLOGY

Snowmelt duration was about 1 month in each year, commencing in mid-April 1992 (Fig. 2) and in mid-May 1993 and was the dominant hydrologic event. In 1992, much higher than normal precipitation occurred during the summer, which contributed 40% of the total annual input to the watershed. In 1993, meltwater was 3 times that in 1992, but summer precipitation contributed only 5% to the total input, which was 2 times higher than in 1992. Runoff from the beginning of snowmelt through August was 60 and 52% of the total annual input in 1992 and 1993, respectively.

The melting rate of the snowpack varied diurnally and was asymmetrical, increasing rapidly to a maximum at the onset of daily melt followed by an attenuated decrease. In addition, daily timing of melt shifted slightly as melting progressed having progressively earlier minima and maxima, and the timing shift is attributed to a progressive increase

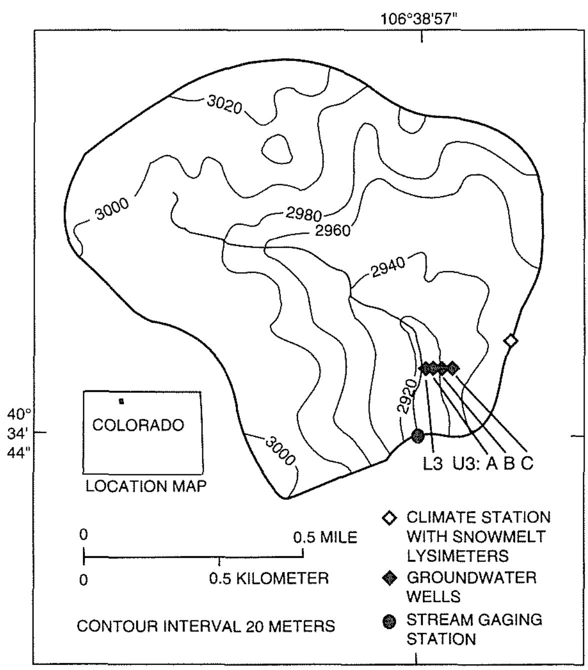

Fig. 1 Location of sampling stations at the Rabbit Ears Pass watershed.

Table 1 Characteristics of the watershed at Rabbit Ears Pass, Colorado, USA.

Component	Characteristic
Drainage Area	2 km^2
Elevation	2910 to 3035 m a.s.l
Air Temperature	Daily average for July 19.7°C, for January -3.9°C
Geology	Bedrock overlain by thin deposits (<4m) of glacial drift Small areas of exposed bedrock are quartz monzonite, granodiorite, and quartz diorite
Vegetation	30% forested (Engelmann spruce and lodgepole pine, scattered stands of aspen) Remainder covered with grass and shrubs
Annual Precipitation Snowpack	Average (1988-93) 925 mm (>95% snow) Maximum Snowpack Water Equivalent: 524 and 940 mm in 1992 and 1993, respectively
Runoff	Average (1988-93) 638 mm Stream channel marked by several beaver dams

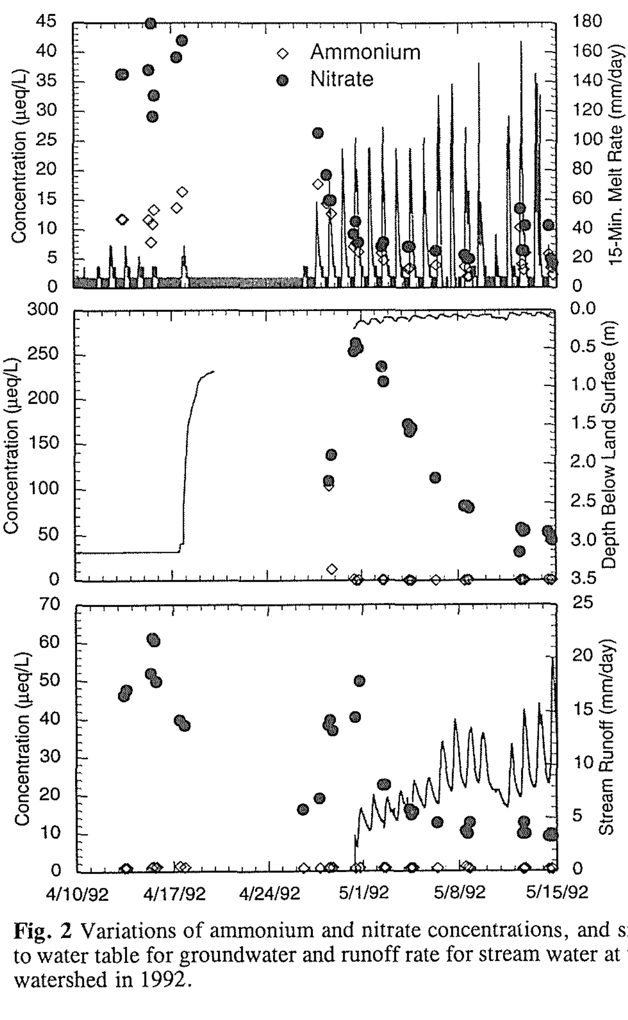

Fig. 2 Variations of ammonium and nitrate concentrations, and snowmelt rate, depth to water table for groundwater and runoff rate for stream water at the Rabbit Ears Pass watershed in 1992.

in the incident solar radiation. Streamflow varied diurnally and displays a similar pattern to that of snowmelt, but variations were much less marked. Streamflow peaked about 2 h after the peak snowmelt and decreased to 60-70% of the peak flow about 18-19 h later. Groundwater levels also varied diurnally, but were more attenuated than that of streamflow (Fig. 2), and the time of daily maximum at the lowest elevation well coincided with the streamflow maximum. Hence, diurnal streamflow variations were attributed to groundwater discharge which varied diurnally and was supplied from snowpack melting.

MELTWATER CHEMISTRY

As observed in many other studies (Johannessen & Henriksen, 1978; Brimblecombe *et al.*, 1985; Tranter *et al.*, 1986; Rascher *et al.*, 1987; Jones, 1988; Stottlemyer, 1990), all major solutes were differentially eluted in meltwater from the snowpack, with highest concentrations occurring at the beginning of the snowmelt period, mid-April 1992 or mid-May 1993. Concentration factors for all major ions as in Tables 2 and 3 except silica, calculated by dividing maximum by mean concentration, ranged from 2.6 to 5.5. in 1992 and 2.4 to 8.3 in 1993. Higher factors in 1993 are consistent with the deep snowpack. Dominant ions in meltwater were Ca^{2+}, NO_3^- and SO_4^{2-}. Also, concentrations of these solutes in meltwater varied diurnally with maxima at the onset of daily melt and with minima at maximum snowmelt. Concentrations of SO_4^{2-} were highly correlated with NO_3^-; for each year, slope and r^2 of a linear regression of SO_4^{2-} on NO_3^- were 1.30 and 0.85, respectively.

Table 2 Solute fluxes during snowmelt 1992 at Rabbit Ears Pass, Colorado.

Constituent	1992 Flux[1] – (from 10 April to 3 August 1992)			
	Streamwater	Meltwater[2]	Precipitation[3]	Net
Water	453.	484.	275.	-306.
H^+	0.2	1.2	4.6	-5.6
NH_4^+	0.4	3.5	2.5	-5.6
Na^+	16.4	0.8	0.6	15.0
K^+	5.8	1.3	0.1	4.4
Mg^{2+}	11.2	3.1	0.4	7.7
Ca^{2+}	30.3	10.0	1.9	18.4
Cl^-	1.6	1.6	0.6	-0.6
NO_3^-	4.5	6.2	3.4	-5.1
SO_4^{2-}	8.7	6.6	4.8	-2.7
SiO_2	43.9	0.0	0.0	43.9

[1] Flux in meq m^{-2}, except dissolved SiO_2 in mmol m^{-2} and water in mm.

[2] Meltwater does not include 241 mm of precipitation from 15 May to 25 August.

[3] Summer precipitation estimated from wetfall at an adjacent NADP site (CO97: 3234 m a.s.l. near Buffalo Pass, 40°32'16" N Latitiude 106°40'35" W Longitude)

Table 3 Solute fluxes during snowmelt 1993 at Rabbit Ears Pass, Colorado.

Constituent	1993 Flux[1] – (from 1 May to 3 August 1993)			
	Streamwater	Meltwater[2]	Precipitation[3]	Net
Water	782.	1434.	77.	-729.
H^+	0.3	5.4	1.3	-6.4
NH_4^+	1.7	9.2	0.7	-8.2
Na^+	34.0	1.6	0.2	32.2
K^+	7.0	1.0	0.0	6.0
Mg^{2+}	24.5	1.0	0.1	22.9
Ca^{2+}	67.5	10.7	0.5	56.3
Cl^-	3.8	2.8	0.2	0.8
NO_3^-	7.9	14.0	1.0	-7.1
SO_4^{2-}	15.8	12.5	1.3	2.0
SiO_2	87.9.	0.0	0.0	87.9

[1] Flux in meq m^{-2}, except dissolved SiO_2 in mmol m^{-2} and water in mm.
[2] Meltwater does not include 77 mm of precipitation from 15 June to 31 August.
[3] Summer precipitation estimated from wetfall at an adjacent NADP site (CO97: 3234 m a.s.l. near Buffalo Pass, 40°32'16" N Latitiude 106°40'35" W Longitude).

GROUNDWATER CHEMISTRY

Groundwater was dominated by Ca^{2+} and generally HCO_3^-, as indicated by alkalinity. Concentrations of weathering products (SiO_2, alkalinity, and base cations) increased down gradient, consistent with an increase in water residence time. However, Ca^{2+} concentrations were balanced by NO_3^- in the highest-elevation well (U3C), which was unexpected. The lower elevation wells are in relatively open areas, but well U3C is adjacent to a small grove of conifers which could affect soil solutions or soil chemistry, or attract fauna that could affect N cycling.

In well U3C, high NO_3^- and Ca^{2+} concentrations (~ 120 and $\sim 250\ \mu$eq l^{-1} in 1992 and 1993, respectively) were observed in each year, which typically decreased markedly by the end of sampling in mid-summer; for 1992 and 1993, NO_3^- concentrations decreased to 16 and 45 μeq l^{-1}, respectively, and Ca^{2+} decreased to 80 and 90 μeq l^{-1}, respectively. In contrast, alkalinity, for which minima were 25 and 65 μeq l^{-1} for 1992 and 1993, respectively, increased with a much smaller absolute change, i.e. 20 and 40 μeq l^{-1} in 1992 and 1993, respectively. Concentrations of most other constituents were relatively constant. Processes that generated NO_3^- either affected Ca^{2+} directly, or if the process was nitrification, the H^+ generated by it was immediately neutralized through a combination of exchange for base cations, mainly Ca^{2+}, and neutralization by alkalinity.

STREAM-WATER CHEMISTRY

Concentrations of NH_4^+, NO_3^-, SO_4^{2-}, and Cl^- in stream water generally were much lower than those of solutes derived from weathering. Compared to meltwater, stream-water NH_4^+ concentrations were low (1.5 compared to 8.5 μeq l^{-1}); NO_3^- concentrations were similar (14 μeq l^{-1}); and SO_4^{2-} and Cl^- concentrations were higher. Stream-water NO_3^- concentrations were comparable to those of groundwater except for the upslope well. Stream-water NH_4^+ concentrations also were comparable to groundwater, and SO_4^{2-} and Cl^- concentrations were lower. Low concentrations of NH_4^+ in both stream water and groundwater compared to meltwater suggests rapid assimilation. Alkalinity, silica, and base cation concentrations in stream water decreased due to dilution by meltwater as snowmelt progressed. Concentrations of each base cation were highly correlated with alkalinity typically with $r^2 > 0.8$; the slope and r^2 for a linear regression of Ca^{2+} concentration on alkalinity for the stream water for individual years were 0.64 and 0.74, respectively. In addition, SO_4^{2-} concentrations were highly correlated with NO_3^-; the slope and r^2 of a linear regression of SO_4^{2-} on NO_3^- were 0.58 and 0.73, respectively.

MASS BALANCE

Atmospheric water flux to the watershed (meltwater plus precipitation) from the beginning of snowmelt to the end of August in 1992 was 50% of that in 1993 (Tables 2 and 3). Yet, differences in the atmospheric inputs of NH_4^+ and NO_3^- were not directly proportional to differences in water flux; NH_4^+ and NO_3^- inputs were 6.0 and 9.6 meq m^{-2} in 1992, respectively, and 9.9 and 15.0 meq m^{-2} for 1993. The atmosphere is an important source of NH_4^+, NO_3^-, SO_4^{2-} and Cl^- and the watershed is the major source of base cations and silica. The percentage of total transport associated with water and N species inputs, however, were comparable in each year; 50% of NO_3^- deposition and 80% of NH_4^+ deposition were retained. Results indicate that some N transport occurred, but the watershed also removes most of N inputs. In contrast, the watershed retained SO_4^{2-} and Cl^- in 1992 (24 and 27%, respectively), and yielded an excess in 1993 (12 and 21%, respectively). Combining the fluxes for 1992 and 1993, SO_4^{2-} and Cl^- input (meltwater plus precipitation) approximately balance stream-water output.

CONCLUSIONS

Snowmelt is the principal hydrologic event in this subalpine watershed in that it generates streamflow for 3 months from a 1-month snowmelt period. Solutes are preferentially eluted from the snowpack and their concentration decreases are partially reflected in stream water, although considerable alteration occurs to meltwater as it travels along shallow hydrologic pathways through surficial material to the stream. Annual stream transport of most solutes was controlled primarily by streamflow and not variations in concentration. A watershed mass balance for 1992 and 1993 indicates that: (1) a major percentage of the primarily atmospherically derived N-species are retained by the watershed, (2) the watershed is the major source of base cations and SiO_2, and (3) for the entire period, atmospheric deposition balances stream-water transport of SO_4^{2-} and Cl^-.

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